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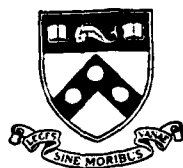
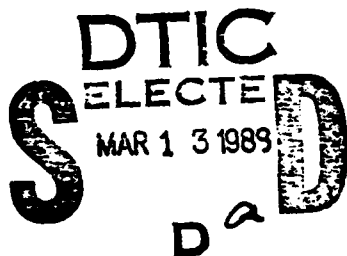
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SIXTH QUARTERLY R&D STATUS REPORT

Principal Investigator:
Alan G. MacDiarmid
Department of Chemistry
University of Pennsylvania

REPORTING PERIOD: 1/1/88 - 3/31/88

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UNIVERSITY of PENNSYLVANIA

PHILADELPHIA, PENNSYLVANIA 19104

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ARPA ORDER NO.: a400004df301

PROGRAM CODE NO.: 6103

CONTRACTOR: Trustees of the University of Pennsylvania
Office of Research Administration
Suite 300 Mellon Building
133 S. 36th Street
Philadelphia, PA 19104-3246

CONTRACT NO.: N00014-86-K-0766

CONTRACT AMOUNT: \$9,420,613

EFFECTIVE DATE
OF CONTRACT: 9/15/86

EXPIRATION DATE
OF CONTRACT: 9/14/91

TELEPHONE NO.: 215-898-8307 or 215-898-6323

SHORT TITLE OF WORK: **Conducting Electronic Polymers by
Non-Redox Processes**

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I. Research Groups*

1. University of Pennsylvania
 - (a) Department of Chemistry (A.G. MacDiarmid)
 - (b) Department of Materials Science (G.C. Farrington)
2. The Ohio State University
Department of Physics (A.J. Epstein)
3. Lockheed Advanced Aeronautics Corporation
Aeronautics Systems Group Research (T.S. Kuan)
4. Rensselaer Polytechnic Institute
Department of Chemistry (G.E. Wnek)
5. University of Rhode Island
Department of Chemistry (S.C. Yang)
6. Montclair State College
Department of Chemistry (B.D. Humphrey)

*Financial information for each group given in Section X.

II. Description of Progress

1. University of Pennsylvania

a. Department of Chemistry (MacDiarmid)‡

(i) Summary of Progress

Polyaniline: Protonation/Deprotonation of Amine and Imine Sites*

→ A model describing the dependence of the protonation level and the oxidation potential of polyaniline as a function of pH of equilibration and oxidation state has been derived. It is assumed that amine and imine sites do not function independently. Predictions are compared with previous experimental data.

*Supported in part by URI and in part by NSF Grant No. DMR-85-19059.

Polyaniline: Doping, Structure and Derivatives*

Redox titration results and electronic spectral evidence show that the oxidation state of the "emeraldine" base form of polyaniline can vary depending on whether its synthesis is performed in the presence or absence of air. Chemical doping of leucoemeraldine, the completely reduced form of polyaniline, to selected oxidation states can be accomplished by a variety of oxidizing agents such as Cl_2 , $(\text{NO})^+(\text{PF}_6)^-$, FeCl_3 , SnCl_4 and TCNQ.)

*Supported in part by URI and in part by NSF Grant No. DMR-85-19059.

Electrochemistry of Ring-Substituted Polyanilines: Effect of Substituents on Electronic Properties*

Poly(o-methylaniline) and poly(o-ethylaniline) have been synthesized by chemical as well as electrochemical methods from the corresponding monomers. The polymers were characterized by elemental analysis, UV-visible spectroscopy and cyclic voltammetry. Upon treatment with 1M HCl, the conductivity of the polymers increased from $\sim 10^{-8}$ S/cm to $\sim 10^{-1}$ S/cm for poly(o-methylaniline) and to $\sim 10^{-3}$ S/cm for poly(o-ethylaniline). The conductivities, optical spectra and electrochemical behavior of the o-alkylsubstituted polymers are compared with those of polyaniline. The

‡In collaboration with Professor A.J. Epstein, Department of Physics, The Ohio State University.

differences are attributed primarily to the steric effect of the alkyl substituents, which alter the torsion angle between the $-C_6H_4-$ rings of the polymer.

*Supported in part by URI and in part by NSF Grant No. DMR-85-19059.

(ii) Major Equipment Purchased or Constructed

Purchased Fisher Super Computer aided Titrimeter.
Purchased Keithley Programmable Current Source, Digital Multimeter and a Vacuum Atmosphere Dry Box for N. Theophilou's research.

b. Department of Materials Science and Engineering
(Farrington)

Summary of Progress

Jonathan Foreman continues his investigations of the reductive (n-doping) electrochemistry of polyacetylene with a focus on the new oriented and ultrapure forms of the material prepared by Nick Theophilou.

Hong Yang has found that network PEO takes up a far smaller concentration of divalent cation salts than linear PEO. This could either be the result of unfavorable partition of the salt between the non-aqueous solvent used to dope the PEO or of some more fundamental structural difference between linear PEO and the network form which leads to less favorable divalent cation solvation in the network form. Either way, the result is intriguing and will be pursued. Hong Yang is also continuing her studies of linear PEO electrolytes containing Zn(II). These materials are particularly interesting because of their potential application as Zn(II) conductors in high energy density batteries.

Kimmy Wu has completed the computerization of our electrochemical equipment, particularly for making electrochemical diffusion measurements on conducting polymers by the potential relaxation technique. Also underway is the development of instrumentation for microelectrode studies of diffusion and electrochemical reactions in solid polymer electrolytes.

2. The Ohio State University

Department of Physics (Epstein)[‡]

(i) Summary of Progress

We have completed our experimental study of the temperature dependent audio-frequency (10^1 - 10^5 Hz) conductivity as a function of protonation level ($0.0 \leq x \equiv [H^+]/[N] \leq 0.08$) of the emeraldine polymer. The dc conductivity varies from 10^{-10} S/cm for $x=0$ to 10^{-6} S/cm for $x = 0.8$ and is proportional to $\exp [-(T_0/T)^{1/4}]$ with T_0 decreasing with increasing x . The temperature dependent audio-frequency conductivity varies as f^s with $s \sim 0.9$ for $x = 0$, decreasing with increasing x . For frequencies greater than 10^3 Hz the dielectric constant agrees with the T independent dielectric constant measured by microwave techniques. At lower frequencies and high temperatures, the dielectric constant increases. A Cole-Cole analysis shows the presence of primarily a single thermally activated relaxation process in these materials. These results are inconsistent with the Kivelson type interpolaron hopping between polaron and bipolaron sites. It is proposed that the dominant mechanism involves pair-wise hopping of charges among polaron and bipolaron sites in the primarily "unprotonated" regions of the emeraldine base polymer. The high frequency (10^5 Hz) dielectric constant can be accounted for by a term related to the contribution of isolated polarons and bipolarons oscillating about their pinning center. Using $\epsilon_p = (4\pi/3\epsilon_0) (n_p/V) (e^2/m_p^* \omega_0^2)$ where $n_p = x$ as the number of polarons per ring, V the volume per ring, m_p^* the polaron effective mass, and ω_0 the polaron pinning frequency, we obtain a pinning energy of 0.3 eV. The polarons and emeraldine are substantially more pinned than solitons and polyacetylene.

The high temperature very low frequency dielectric constant can be analyzed within a model of charge hopping among polarons sites. We use a classical dipole model to estimate the contribution to the dielectric constant of this interpolaron hopping:

$$\epsilon = \frac{4\pi}{\epsilon_0} \left[\frac{n_p}{A} \right] \left[\frac{n_{bp}}{n_p + n_{bp}} \right] \frac{e^2 L^2}{k_B T} \left[\frac{1}{1 + \omega^2 \tau^2} \right]$$

[‡]In collaboration with Professor A.G. MacDiarmid, Department of Chemistry, University of Pennsylvania.

Here n_p is the number of polarons per ring of the polymer, n_{bp} the number of bipolarons per unit length of the polymer, A the cross-sectional area of bipolaron chain, L^2 the mean square average hopping distance between polarons. Assuming a density of one polaron per 500 rings (or an average 50Å apart) this equation can be solved in the $\omega \leq \tau$ limit to give the fraction of bipolarons in the polymer. The experimental low frequency value of $\epsilon = 12$ implies a concentration of approximately 3.7×10^{-3} bipolarons per polaron for $x = 0$ increasing to approximately 1.1×10^{-2} for the $x = 0.017$ sample with average separation between polarons of 42Å. These low concentrations of bipolarons are reasonable in the context of available data on the polymer. For $x = 0.08$, this model (with an average separation between polarons of 33Å) assuming negligible contribution from the isolated metallic islands being formed, gives a concentration of 7.9×10^{-2} bipolaron per polaron. Thus, the dielectric constant can be understood within a picture of three-dimensional charge hopping among polaron sites. It is noted that the near-identical value of effective activation energy obtained for τ from dielectric constant and σ_{dc} supports this picture.

The dielectric constant data clearly distinguishes two different behaviors for emeraldine polymers, that for polymers of composition $x \leq 0.13$ and that for those of composition $x \geq 0.22$. We concentrate first on the lightly protonated samples. The microwave and 10^5 Hz measured dielectric constants are the same to within experimental error. The contribution of the dielectric constant that is frequency and temperature independent to 6×10^9 Hz is likely due to electronic polarization of the emeraldine backbone. The small increase in ϵ with protonation may reflect the contribution of isolated polarons and bipolarons formed at these doping levels oscillating about their pinning center. Assuming a pinning model and averaging the dielectric constant over three directions,

$$\epsilon_p = \frac{4\pi}{3\epsilon_0} \frac{n_p}{V} \frac{e^2}{m_p^* \omega_0^2}$$

where $n_p = x$ is the number of polarons per ring, V the volume per ring, m_p^* the polaron effective mass, and ω_0 the polaron pinning frequency. For $x = 0.13$, using $V = 125\text{\AA}^3$, $\epsilon_p = \Delta\epsilon = (6.7-3.5)=3.2$, and $m_p^* \sim 50m_e$ from photoinduced ir studies, we obtain $\omega_0/2\pi = 4.6 \times 10^{13}$ Hz or a pinning energy of 0.19 eV. Thus the polarons in emeraldine are substantially more pinned than the solitons in polyacetylene. This is in accord with the amplitude mode formalism analysis of the photoinduced and dopant induced infrared activity in emeraldine. The large

value of $\sigma_{\mu\omega}$ compared to σ_{DC} for $x \leq 0.13$ at all T reflects the existence of some more probable hops that do not contribute to dc conductivity.

For higher protonation levels, the increase of the dielectric constant with temperature is an indication of presence of potential barriers for polarizable species. A single relaxation process will yield Drude-like behavior for dielectric constant $\epsilon = \epsilon_{\text{background}} + \epsilon_{\infty} + (\epsilon_{dc} - \epsilon_{\infty}) / (1 + \omega^2\tau^2)$ where $\epsilon_{\text{background}} \equiv 5$ as measured for emeraldine base. ϵ_{dc} is the limiting value for $\omega = 0$ or $\tau = 0$ and ϵ_{∞} is the high frequency limit. An activated relaxation process $\tau = \tau_0 \exp(\Delta/T)$ provides a model that accounts for $\epsilon(T)$. An $\epsilon(T) \propto T$ can be understood assuming a distribution of barrier potentials $\Delta_{\min} < \Delta < \Delta_{\max}$ and a probability function belonging to one of the Dyson's classic axioms in random diffusion problems. Stronger T -dependence of ϵ with increasing x may reflect a change in distribution of Δ 's with increasing protonation. In the limit of $T = 0$, the dielectric constant will approach $\epsilon_{\text{background}} + \epsilon_{\infty}$ irrespective of the frequency of measurement. Therefore observation of two different zero temperature asymptotes for $[C]/[N] > 0.13$ and < 0.13 indicates the presence of more polarizable species for intermediate to highly protonated samples.

A likely origin of ϵ in the intermediate to highly protonated regime is the effect of disorder on the motion of charge carriers. Assuming one dimensional motion within a model of strands of metal wire

$$\epsilon = \frac{4\pi}{\epsilon_0} e^2 l_i^2 n(E_F)$$

where l_i is the effective coherence lengths ("mean free path") of charge carriers and $n(E_F)$ is the density of states at the Fermi level. From our magnetic susceptibility measurement we estimate $n(E_F) \sim 1.5$ states/eV-ring for $x = 0.50$ protonated emeraldine salt. A low T effective mean free path of $\sim 0.7 \text{ \AA}$ is calculated for $x = 0.50$ for a measured $\epsilon \sim 15$. Due to the presence of the depolarization effect in three dimensional systems, the dielectric constants reported here for the polyaniline salts are smaller than (expected) microscopic values for one dimensional strands of wires. Therefore the value of the coherence length of the order of 0.7 \AA is an underestimate. The increase of dielectric constant with increasing temperature is again the result of increase of the effective localization length with temperature.

The effective mean free path may be used to estimate a value for conductivity within the "metal islands" at low temperatures. Assuming free carrier motion of electrons of mass m_e within a half filled polaron band of width $(4t_0)$ 0.4 eV from our χ^P and lattice repeat unit, a , of 10 Å, the Fermi velocity is $v_F = 2t_0a/h \approx 3.0 \times 10^7$ cm/s and $\tau = l_i/v_F \approx 2.3 \times 10^{-16}$ s. If all electrons in the polaron band contribute to the conductivity, $\sigma = ne^2\tau/m$ implies "intrinsic" conductivity within the "metallic islands" of ~ 250 S/cm at low temperatures. Increasing effective mean free path with increasing T would lead to higher intrinsic conductivity at more elevated temperatures.

We note that the protonated emeraldine form of polyaniline shows a large electric loss tangent at the microwave frequency of measurement. Moreover, this loss tangent increases monotonically with protonation level of the polymer. At room temperature for $x = 0.22$, $\tan \delta = \epsilon''/\epsilon' \sim 0.8$ increasing to ~ 1.5 for $x = 0.30$ and further to a value of ~ 2.3 for $x = 0.50$. Moisture increases both the microwave conductivity and the dielectric constant of $x = 0.50$ emeraldine salt such that the loss tangent of a fully protonated emeraldine polymer under dynamic vacuum increases by a factor of ~ 3.5 upon exposure to moisture. The values of the loss tangent should be compared to the value of ~ 1.2 for commercially available carbon-filled insulating polymers. Variation of the loss tangent with protonation level of emeraldine polyaniline makes this polymer a very fascinating material.

With increasing protonation much beyond the $x = 0.1$ level, it is expected that the charge conduction becomes dominated by interaction among the granular metal islands formed. The bipolaron/polaron hopping conduction mechanism is quite general and may be appropriate for other lightly doped non-degenerate conjugated polymers, for example, polypyrrole, polythiophene, polyparaphenylene, and polyparaphenylenesulfide.

We have studied the optical absorption of emeraldine base dissolved in NMP solutions. There are small red shifts in both the 2.0 and 3.8 eV absorption peaks ongoing from the film to solution in NMP. The origin of this red shift may be due to different ring conformations. A thermochromatic effect was observed for the first time in the emeraldine base solutions. There is a blue shift with increasing temperature $\Delta E/\Delta T \sim 1$ meV/K. Similar size effects are seen in the solid film. In comparison with other systems, the emeraldine polyaniline is the first system that exhibits the thermochromatic effect without side groups. The photoinduced absorption spectra of emeraldine base solutions in NMP was acquired from 0.5 eV to 3.3 eV using a chopping frequency of 21 Hz and lower power density of 400 mW/cm². The photoinduced spectra saw similar results

with emeraldine in different solvents. There is a constant bleaching across the entire spectrum which, we believe, is attributable to heating effects. In comparison with the photoinduced absorption solid film, there is a 1.4eV and 3.0eV photoinduced absorptions and 1.8eV photoinduced bleaching as in the film, while the 0.9eV peak absorption in the film is absent in solution form. The appearance of the 0.9eV peak is of paramount importance in distinguishing the origins of the photoinduced excitations. The 0.9eV peak in the solid films has a more rapid decay time than the 1.4eV photoinduced absorption. The absence of the 0.9eV photoinduced absorption in solution clearly demonstrates that the 0.9eV excitations form a three dimensional or interchain interaction. One likely candidate is the formation of a new type of interchain bipolaron.

The temperature dependence of the x-band electron spin resonance for the emeraldine oxidation state of polyaniline is under investigation as a function to different protonation levels and means of sample treatment. We found the line-width varies with sample treatment. In addition, the lines are decomposable into a sum of Lorentzian and Gaussian signal.

We have applied the microwave cavity perturbation technique at 6.4 GHz to study the effects of local order on the microwave properties of other one-dimensional systems, especially three tetramethyltetrathiofulvalene salts: $(\text{TMTTF})_2\text{X}$, X-SCN, ReO_4 , and SbF_6 . A divergence of the dielectric constant ϵ is observed at the structureless transition temperature for SbF_6 (160K) and ReO_4 (220K), contrasting with a stepwise change at the anion ordering transition of the latter salt (160K). The dielectric constant of $(\text{TMTTF})_2\text{SCN}$ shows a broad maximum above the anion ordering transition and a sharp decrease at T_c . Moreover, the microwave conductivity exceeds dc conductivity above the structureless transition in $(\text{TMTTF})_2\text{SbF}_6$. Also, conductivity becomes frequency dependent below the anion ordering of $(\text{TMTTF})_2\text{SCN}$. These data support the pseudogap picture describing the structureless transition, a complete gap for the anion ordering transition, and the absence of charge-density waves in these materials.

(ii) Major Equipment Purchased or Constructed

Miscellaneous infrared and optical components were purchased. These items include mirrors, shutter controls, translational stages, substrates, lamps, lenses, beam splitters, and windows. A heat exchanger was purchased to provide cooling for the argon laser.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

Summary of Progress

Lockheed did not receive funding for research from the URI during this quarter, therefore due to government regulations they were unable to work on URI sponsored research during this period. Therefore, they can not legally state any progress.

4. Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

Summary of Progress

Our collaborative work with the University of Lowell (VEH calculations) has established that the experimentally observed visible spectra of "segmented" polyacetylene is inconsistent with the idea of random defect placement. We proposed at a URI joint group meeting in Somerset in October, 1986, that clustering of defects is anticipated based on kinetic and thermodynamic arguments. In other words, conjugation lengths in "segmented" polyacetylenes are longer than predicted simply from knowledge of the defect composition. Our proposal has been summarized along with the Lowell work in a recent publication (S. Clough, S. Tripathy, X. Sun, B. Orchard and G. Wnek, "Comment on the Introduction of Defects into Polyacetylene: Random vs. Non-Random Placement," Makromol. Chem., Rapid Commun., in press).

Dr. Walter Focke summarized his ideas concerning the issue of capacitative currents in polyaniline cyclic voltammograms in a recent paper (W.W. Focke and G.E. Wnek, "Conduction Mechanisms in Polyaniline (Emeraldine Salt)", J. Electroanal. Chem. Electrochem., submitted) and concludes that a hopping mechanism best describes electronic conduction in polyaniline. We anticipate the paper to be accepted after responding to minor comments of a referee.

Professor Wnek has reviewed the area of charge carrier chemistry of conductive polymers. Charge carrier generation has been likened to the initiation step in ionic polymerization of vinyl monomers (G.E. Wnek, "Charge Carrier Chemistry in Electroactive Polymers," Proceedings of the IUCCP Symposium on Functional Polymers, Texas A&M University, Plenum, in press). Analogies between carrier propagation and termination reactions were made,

with the conclusion that "stable" charge carriers should exhibit the characteristic or propagating ends in "living" polymerization.

Dr. J.J. Lee, a biochemist in Professor Wnek's group, began an investigation of complex formation between histone H3 and poly(styrene sulfonate) in aqueous buffers. She is supported by RPI but works closely with Lynette Prezyna. We have found that H3 (MW = 16kD) forms soluble complexes with PSS (MW = 16kD) up to PSS/H3 ratios of ~1:1. PSS appears to engulf H3 as treatment of the complex with the enzyme trypsin does not afford peptide fragments. It will be interesting to compare the behavior of the complexes formed from soluble PSS to those from "two-dimensional" conductive polymer films containing sulfonate anions.

5. University of Rhode Island

Department of Chemistry (Yang)

Summary of Progress

The third project listed in the fifth quarter report is still on hold because we still do not have any money for this year. The research activities in this quarter are again mainly in the area partially supported by an industrial grant.

Morphological modification of polyaniline:

We have made progress on the verification of our proposed model of template controlled morphology. Analysis of the composition of the morphologically modified polyaniline is in progress. We found that the template-dependent morphological modification is consistent with the varied modes of monomer/template interaction and the varied strength of the interaction.

Kinetics of electrochemical doping:

We have begun to study the effect of surface morphology of polyaniline on the kinetics of the structural transformations when thin film polyaniline is subjected to a step function of the electrochemical doping. We have studied samples of different substrate electrodes which have different surface morphology. A large difference in the rate constants is found for polyanilines coated on different substrates. The corresponding difference in polymer morphology was examined by electron microscopy.

6. Montclair State College

Department of Chemistry (Humphrey)

(i) Summary of Progress

Considerable progress was made during this quarter on the use of different oxidizing agents (polymerization initiators) and the effect these initiators have on the formation of conducting polymer/polysaccharide composites. Preliminary results indicate that the amount of bonded conducting polymer in the composites is dependent upon the oxidizing agent used in the synthesis. Also the degree of penetration of the conducting polymer into the polysaccharide matrix is dramatically affected by the polymerization initiator used. In particular, ceric (IV) ions are known to generate graft polymerization sites in cellulose. When ceric ammonium sulfate is used as an oxidant in the formation of these composite materials the conducting polymers are incorporated in the interior of the matrix almost exclusively. Evidence for this conclusion is supported by conductivity experiments.

(ii) Major Equipment Purchased or Constructed

A Nicolet Fourier Transform Infrared Spectrometer equipped with a diffuse reflectance attachment was installed. This apparatus should prove useful for further investigation and characterization of the new composite materials.

III. Working Relationships Involving University of Pennsylvania Personnel and Those of Subcontractors

The following interactions between personnel funded by the URI contract have taken place during this quarter:

February 19-21, 1988, A joint group meeting was held at New Stanton, PA, between members of Dr. A.G. MacDiarmid's group, Dr. G.C. Farrington and several members of Dr. A.J. Epstein's group.

IV. Miscellaneous Scientific Interactions of Key Personnel Associated with the Program involving (i) visits to their laboratories by persons concerned with conducting polymers, (ii) visits by them to other laboratories and (iii) lectures on their research at organized symposia.

1. January 4, 1988, Mr. J. Masters of the University of Oklahoma, Norman, OK, visited the laboratory of Dr. A.G. MacDiarmid.
2. January 6, 1988, Dr. P. Vasubevan, Indian Institute of Technology, Delhi, India, visited the laboratory of Dr. A.J. Epstein at OSU. She discussed future uses of electro-active polymers.
4. January 8, 1988, Dr. Kumar Patel, AT&T Bell labs, Murray Hill, NJ, visited the laboratory of Dr. A.J. Epstein at OSU. Title of talk given: "Why All the Excitement in Superconductivity?"
5. January 9, 1988, Dr. G.E. Wnek gave an invited lecture at California State University, Los Angeles, CA, entitled "Charge Carrier Chemistry in Electroactive Polymers."
6. January 12, 1988, , Ongoing collaboration begun with Dr. Y. Wei of Drexel University, Philadelphia, PA, formerly of Dr. G. Wnek's group at MIT.
7. January 26-27, 1988, Dr. Terry Gustafson, B.P. America Research and Development, Warrensville, OH, visited the laboratory of Dr. A.J. Epstein at OSU. Title of talk given: "MHz Amplification of the Synchronously-Pumped Dye Laser: Quasi-CW and Time-Resolved Applications."
8. January 22, 1988, Dr. Epstein, Dr. R. McCall, Dr. G. Roe, and J. Ginder visited Batelle Memorial Institute in Columbus, OH, to discuss possible collaboration on nonlinear optical properties of conductivity polymers. Dr. Epstein presented a talk entitled "Non-Linear Optical Phenomena in Conductive Polymers: Polyaniline."
9. February 3-5, 1988, Dr. Epstein visited DuPont de Nemours in Wilmington, DE to discuss joint polymer research.
10. February 11, 1988, Dr. Robert Grimm, Edison Welding Institute, Columbus, OH, visited the laboratory of Dr. A.J. Epstein at OSU. He discussed applications of conducting polymers with Dr. Epstein.

11. February 12, 1988, Professor David Tanner, University of Florida, Gainesville, FL, visited the laboratory of Dr. A.J. Epstein at OSU. Title of talk given: "Optical Properties of High-Temperature Superconductors."
12. February 16, 1988, Professor Robert Metzger, University of Alabama, Tuscaloosa, AL, visited the laboratory of Dr. A.J. Epstein at OSU. Title of talk given: "Langmuir-Blodgett Films of Potential Organic Rectifiers."
13. February 17, 1988, Dr. Robert Schwerzel and coworkers, Batelle Memorial Institute, Columbus, OH, visited the laboratory of Dr. A.J. Epstein at OSU. He discussed possible joint work on nonlinear optical properties of polyaniline.
14. February 18, 1988, Dr. Epstein visited Ford Research Laboratories in Dearborn, MI. He presented a talk entitled "New Concepts in conducting Polymers: Polyaniline."
15. February 24 & 25, 1988, Dr. A.G. MacDiarmid and Dr. A.J. Epstein attended Executive Committee Meeting at Los Alamos, NM, for ICSM '88 (International Conference on Synthetic Metals).
16. March 4, 1988, Dr. Epstein visited Xerox Corporation in Rochester, NY to discuss joint polymer research with Dr. E. Conwell and Dr. C. Duke.
17. March 7-10, 1988, Gordon Conference on Radiation and Macromolecules, Oxnard, CA, Dr. MacDiarmid gave an invited talk entitled "Conducting Polymers: Basic Structural, Doping and Electronic Concepts."
18. March 9, 1988, a Cooperative Research Agreement on Conductive Polymers Research was signed between du Pont Laboratories and Penn and OSU.
19. March 9-11, 1988, Professor Jill Bonner, University of Rhode Island, Kingston, RI, visited the laboratory of Dr. A.J. Epstein at OSU. Title of talk given: "Quantum Spin Chains and High Tc Superconductivity."
20. March 9-11, 1988, Dr. Phil Gurney, Johnson-Matthey Company, England, visited the laboratory of Dr. A.J. Epstein at OSU. He discussed potential uses of polymers and ceramics.
21. March 14-15, 1988, Dr. F.A. Cotton, Texas A&M University, College Station, TX, visited Dr. MacDiarmid's laboratory. Title of talk given, "Spontaneous Self-Assembly: The Synthetic Chemist's Secret Weapon."

22. March 17, 1988, Dr. G.E. Wnek gave an invited lecture at the Electric Power Research Inst., Palo Alto, CA, entitled "Electrically Conductive Polymers: An Overview."

23. March 21-23, 1988, American Physical Society Meeting, New Orleans, LA, following talks given:

- i. A.G. MacDiarmid, S.P. Ermer, A. Ray, E.M. Scherr, A.J. Epstein, H.H.S. Javadi, F. Zuo M. Akhtar and Z. Kiss: "Polyaniline: Synthesis of Films and Their Use in Determining the Absence of Protonic Conductivity in Doped Polyaniline."
- ii. A.J. Epstein, H.H.S. Javadi, R. Laversanne, Y. Cao, J. Gaines, M. Angelopoulos and A.G. MacDiarmid, "Microwave Response of Emeraldine Polymer."
- iii. F. Zuo, A.J. Epstein, M. Angelopoulos and A.J. Epstein, "AC Conductivity of Polyaniline."
- iv. M.G. Roe, J.M. Ginder, R.P. McCall, P.E. Wigen, A.J. Epstein, M. Angelopoulos, A.G. MacDiarmid, "Photoexcitation of Excitons and Polarons in Emeraldine Base."
- v. J.M. Ginder, M.G. Roe, R.P. McCall, Y. Song, J.R. Gaines, E. Ehrenfreund and A.J. Epstein, "Photoexcitations in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-d}$ System."
- vi. H.H.S. Javadi, R. Laversanne and A.J. Epstein, "Microwave Conductivity and Dielectric Constant of $(\text{TMTTF})_2\text{X}$, $\text{X}=\text{SCN}$, ReO_4 , and SbF_6 ."

24. March 23, 1988, Dr. G.E. Wnek attended the IUCCP Symposium on Functional Polymers, Texas A&M University, College Station, TX, gave an invited talk "Charge Carrier Chemistry in Electroactive Polymers."

25. March 27, 1988, Dr. Serge LeFrant, Université De Nantes, France, visited Dr. MacDiarmid's laboratory. Title of talk given, "Raman Spectra of Conducting Polymers with Phenyl Rings."

26. March 28, 1988, Professor F.G.A. Stone of the University of Bristol visited the laboratory of A.G. MacDiarmid. Title of talk given, "The Non-Spectator Role of Carbaborane Groups in the Chemistry of Compounds with Heteronuclear Metal-Metal Bonds."

27. March 29, 1988, Professor Royce Murray, University of North Carolina, Raleigh, NC, visited the laboratory of Dr. A.J. Epstein at OSU. Title of talk given: "Electrochemical Voltammetry Without Liquids."

28. March 30, 1988, Dr. G.E. Wnek gave an invited lecture at Union Carbide Corporation, Bond Brook, NJ, entitled "Charge Carrier Chemistry in Electroactive Polymers."

V. Publications

1. Papers Published

(i) Epstein and/or MacDiarmid (OSU and/or Penn)

"A Covalent Bond to Bromine in HBr Treated Polyaniline From X-Ray Diffraction," Synth. Met. **22**, 191 (1988). B.K. Annis, A.H. Narten, A.G. MacDiarmid and A.F. Richter. (Supported in part by URI and in part by DOE Contract DE-ACO5-84-OR21400).

(ii) Wnek (RPI)

"Reactions of n-type (Reduced) Polyacetylene with Alkyl Halides," Macromolecules, **21**, 266 (1988) D. H. Whitney and G. E. Wnek. (Supported in part by URI and in part by an ARCO Career Development Award).

"Electrochemistry of Polyaniline: Consideration of a Dimer Model," Symp. Proc. Electroactive Polymers, Eds P. Prasad and D. Ulrich, pp. 315, Plenum Press, New York, 1988. W.W. Focke and G.E. Wnek. (Supported in part by URI and in part by the Council for Scientific and Industrial Research of South Africa).

2. Papers Accepted/Submitted for Publication

Acknowledging URI and Other Support

(i) Epstein and/or MacDiarmid (OSU and/or Penn)

"Conduction Mechanism of Polyaniline: Effect of Moisture," Synth. Met., in press (1988). H.H.S. Javadi, M. Angelopoulos, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Solid State ^{13}C NMR Characterization of Polyaniline," S. Kaplan, E.M. Conwell, A.F. Richter and A.G. MacDiarmid. J. Am. Chem. Soc., submitted (1988). (Supported in part by URI and in part by Xerox Corporation).

(ii) Farrington (Penn)

"Studies of the Hydration of Transition Metal Cations Dissolved in Poly(ethylene oxide) by UV/Visible Spectroscopy," J. Electrochem. Soc., submitted (1988), R. Huq, M.A. Saltzberg and G.C. Farrington. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

(iii) Wnek (RPI)

"Comment on the Introduction of Defects into Polyacetylene: Random vs. Non-Random Placement," Makromol. Chem. Rapid. Commun., in press (1988). S. Clough, S. Tripathy, X. Sun, B. Orchard and G.E. Wnek. (Supported in part by URI).

"Charge Carrier Chemistry in Electroactive Polymers," Proceed. IUCCP Symposium on Functional Polymers, Plenum Press, New York, in press (1988), G.E. Wnek. (Supported in part by URI and in part by ONR Contract No. N00014-83-K-0209).

"Conduction Mechanisms in Polyaniline (Emeraldine Salt)," J. Electroanal. Chem. Electrochem., submitted 1988, W.W. Focke and G.E. Wnek. (Supported in part by URI and in part by Council for Scientific Research of South Africa).

(iv) Wnek and MacDiarmid (RPI and Penn)

"Synthesis and Electrochemistry of Alkyl Ring Substituted Polyaniline," J. Phys. Chem. submitted 1988, Y. Wei, W.W. Focke, G.E. Wnek, A. Ray and A.G. MacDiarmid. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

VI. Patents

Patents resulting from URI support

None

VII. Changes in Personnel

1. University of Pennsylvania

a. Department of Chemistry (MacDiarmid)

Dr. David L. Kershner, after receiving his Ph.D. from Northwestern University, Evanston, IL, joined Dr. MacDiarmid's group as a post-doctoral fellow.

b. Department of Materials Science and Engineering (Farrington)

There were no changes in personnel during this quarter.

2. The Ohio State University

Department of Physics (Epstein)

Dr. Mitchell Greg Roe, who graduated last quarter, has changed positions from Graduate Research Associate to Postdoctoral Research Associate as of January 1, 1988. Ms. Cheryl Sievert was employed last quarter as an undergraduate aid to assist with secretarial responsibilities, but is not working this quarter in order to continue her studies. Ms. Joanna Zinkon began working January 20, 1988 as an undergraduate aid to assist with secretarial responsibilities. Ms. Kathy Waugh is no longer working as secretary as of February 5, 1988. Ms. Diana Malone has been employed beginning February 29, 1988.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

There were no changes in personnel during this quarter.

4. Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

There were no changes in personnel during this quarter.

5. University of Rhode Island

Department of Chemistry (Yang)

There were no changes in personnel during this quarter.

6. Montclair State College

Department of Chemistry (Humphrey)

There were no changes in personnel during this quarter.

VIII. Contractual Administration

1. Prime Contract - University of Pennsylvania

Partial funding for \$500,000.00 was received by the University of Pennsylvania, Office of Research Administration, on February 17, 1988. This represents partial funding for the second year of the contract (October 1, 1987 to September 30, 1988).

IX. Miscellaneous

Due to the fact that all funding for Year 2 (October 1, 1987 - September 30, 1988) was not received until June 28, 1988, considerable interruption of research was involved, particularly by Lockheed corporation, due to periods in which Lockheed had no funds. This involved a re-shuffling of research personnel. Although the receipt by the University of Pennsylvania of approximately 1/3 of the total second year budget on February 17, 1988 helped to alleviate this problem, stoppages of research still occurred due in part to the time lag involved between which the University of Pennsylvania received funding and the time by which the administration of the various organizations was able to use the new funding.

**X. Fiscal Status
Expenditures and Commitments**

A. University of Pennsylvania: The following represents monies spent and/or committed to that portion of the program carried on at the University of Pennsylvania.

	1st Year Budgeted 9/15/86-9/30/87	2nd Year Budgeted 10/1/87-9/30/88	New Funding added on 2/17/88	Total Spent & Committed 9/15/86-3/31/88	Available Balance on 3/31/88	Budgeted Balance
U of P (Chem) (Dr. A.G. MacDiarmid)	727,044	577,611	187,466	605,179	309,331	699,476
U of P (MSE) (Dr. G.C. Farrington)	231,565	309,845	102,108	420,398	(86,725)	121,012

B. Subcontracts

	1st Year Budgeted 9/15/86-9/30/87	2nd Year Budgeted 10/1/87-9/30/88	New Funding added on 2/17/88	Total* Spent & Committed 9/15/86-3/31/88	Available Balance on 3/31/88	Budgeted Balance
OSU (Dr. A.J. Epstein)	867,116	369,597	121,800	956,744	32,172	279,969
Lockheed (Dr. T. Kuan)	87,037	87,037	30,732	97,152	20,617	76,922
MM Inc. (Ms. M. Dolton)	37,143	30,246	11,985	49,127	1	18,262
Academic Subcontractors						
a. Dr. Wnek	36,996	0	0	36,796	200	200
1. MIT	36,006	69,940	31,862	33,720	34,148	72,226
2. RPI						
b. Univ. Rhode Island (Dr. S. yang)	31,862	31,862	0	31,862	0	31,862
c. Montclair State (Dr. B. Humphrey)	29,231	31,862	14,047	29,231	14,047	31,862

*The following represents monies paid on receipt of demand (i.e., bills) from participating subcontracts.